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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-176**
Schroer, Thorsten (USC); Christe, K.O. (ERC), "Novel Synthesis of $[\text{ClF}_6]^+$ and $[\text{BrF}_6]^+$ Salts"

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(Deadline: 05 Sep 2000)

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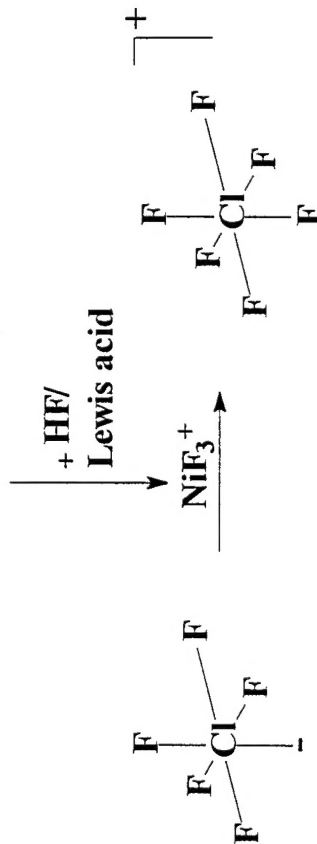
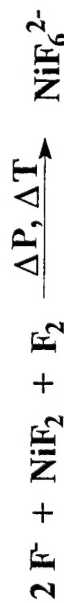
**Thorsten Schroer and
Karl O. Christe***

Inorg. Chem.

Novel Synthesis of $[\text{ClF}_6]^+$
and $[\text{BrF}_6]^+$

SYNOPSIS

The increasing order of oxidizing power from anion to neutral molecule to cation can be used for a convenient synthesis of superoxidizers. This approach is based on the preparation of high oxidation state transition metal fluoride anions by high pressure/high temperature fluorination reactions with elemental fluorine and their conversion into superoxidizing cations by adding strong Lewis acids in anhydrous HF solution. This principle is demonstrated for the synthesis of ClF_6^+ and BrF_6^+ from NiF_3^+ .



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Novel Synthesis of $[\text{ClF}_6]^+$ and $[\text{BrF}_6]^+$ Salts

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Abstract

For a compound in a given oxidation state, its oxidizing strength increases from its anion to the neutral parent molecule to its cation. Similarly, an anion is more easily oxidized than its neutral parent molecule, which in turn is more easily oxidized than its cation. This concept was systematically exploited in our search for new superoxidizers. Transition metal fluoride anions were prepared in their highest known oxidation states by high temperature/high pressure fluorinations with elemental fluorine and subsequently converted to their more strongly oxidizing cations by a displacement reaction with a strong Lewis acid. The application of this principle resulted in new syntheses for $[\text{ClF}_6]^+[\text{AsF}_6]^-$ and $[\text{BrF}_6]^+[\text{AsF}_6]^-$ using the highly reactive and thermally unstable $[\text{NiF}_3]^+$ cation which was prepared from the reaction of the $[\text{NiF}_6]^{2-}$ anion with AsF_5 in aHF. Attempts to prepare the known KrF^+ and ClO_2F_2^+ cations and the yet-unknown XeF_7^+ cation by the same method were unsuccessful. The results from this and previous studies show that $[\text{NiF}_3]^+$ is a stronger oxidative fluorinator than PtF_6 , but whether its oxidizing strength exceeds that of KrF^+ remains unclear. Its failure to oxidize Kr to KrF^+ might have been due to unfavorable reaction conditions. Its failure to oxidize ClO_2F to ClO_2F_2^+ , in spite of its favorable oxidizer strength, is attributed to the high Lewis basicity

of ClO_2F which results in a rapid displacement reaction of NiF_3^+ by ClO_2F , thus generating the weaker oxidizer NiF_4 and the more difficult to oxidize substrate ClO_2^+ . Therefore, the general applicability of this approach appears to be limited to substrates that exhibit a weaker Lewis basicity than the neutral transition metal parent molecule. Compared to KrF^+ or PtF_6 based oxidations, the NiF_3^+ system offers the advantages of commercially available starting materials and higher yields, but product purification can be more difficult and tedious than for KrF^+ .

Introduction

In complex fluorides, the removal of a fluoride ion from the central atom increases its effective electronegativity. Consequently, the oxidizing power of a compound in a given oxidation state increases in the order: anion < neutral molecule < cation, and high oxidation state anions are more stable and can be prepared more easily than the corresponding cations.

The increased accessibility of the anions is well known and has been exploited for the syntheses of the highest oxidation states of transition metal fluorides.¹ It is also well known that the addition of strong Lewis acids to these complex transition metal fluoride anion salts liberates the free parent molecules² which, in turn, can form with an excess of Lewis acid the corresponding complex transition metal fluoride cations.

The combination of these two principles, i. e., the ready synthesis of anions at the limits of oxidation by high pressure / high temperature fluorinations and their subsequent conversion into cations of even higher oxidizing power by acidification, offers the potential for new superoxidizers of unprecedented power. Their power might rival or surpass that of the strongest presently known oxidizer, the $[\text{KrF}]^+$ cation.³

This approach, however, exhibits a general problem. It arises from the fact that frequently the corresponding neutral parent molecule and cation are thermodynamically unstable, ³tending to decompose rapidly to a lower oxidation state fluoride and elemental fluorine. This property has previously been exploited for the first chemical synthesis of elemental fluorine⁴ and for solid propellant fluorine gas generators.⁵ Although the

principle of generating very powerful new oxidizers by acidification of high oxidation state transition metal fluoride anions had been known for many years,^{2,4,5} only ^afew studies have been carried out on the oxidizer strengths of these species. Thus, Bartlett and Žemva were able to oxidize xenon to XeF₆, [RuF₆]⁻ to RuF₆ and [PtF₆]⁻ to PtF₆ by using mixtures of [NiF₆]²⁻ salts and BF₃ or AsF₅ in aHF.^{6,7} Furthermore, mixtures of K₂[NiF₆] and BF₃ in aHF were used as a fluorinating reagent in organic chemistry. For example, CH₃CN reacts under these conditions with formation of CF₃CN and CF₃CF₂NF₂.⁸

The goal of this study was the exploration of the oxidizing strength of NiF₃⁺ and its comparison with those of [KrF]⁺ and PtF₆. Suitable substrates for these studies were ClF₅, BrF₅, XeF₆, ClO₂F and Kr.³ Until now, [ClF₆]⁺ salts were only obtainable from the reactions of ClF₅ with [KrF]⁺ salts⁹ and PtF₆,¹⁰ and [BrF₆]⁺ salts only from the reaction of BrF₅ with [KrF]⁺ salts.¹¹

Experimental Section

Caution! All substances used in this investigation are strong oxidizers and contact with moisture, water or organic materials must be avoided. HF is toxic and can cause severe burns. Protective gear and a face shield must be worn while working with these substances.

Materials and apparatus. All volatile materials were handled in a stainless steel-Teflon FEP vacuum line.¹² This line and all reaction vessels were passivated with ClF₃ prior to use. All nonvolatile materials were handled in the dry argon atmosphere of a glove box.

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Infrared spectra were recorded in the range of $4000 - 400 \text{ cm}^{-1}$ on a Midac FT-IR Model 1720 at a resolution of 1 cm^{-1} . Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range of $4000 - 10 \text{ cm}^{-1}$ on a Bruker Equinox 55 spectrophotometer using a NdYag laser at 1064 nm. Sealed, baked out (10 mtorr, 48 h, 300°C) Pyrex melting point tubes were used as sample containers. ^{19}F NMR spectra were recorded on a Bruker AM-360 instrument at 339 MHz using neat CCl_3F at room temperature as an external standard. Samples were measured in heat sealed 3 mm, i.d. Teflon FEP tubes (Wilmad Glass Co.).

Literature methods were used for the preparation of $\text{Cs}_2[\text{NiF}_6]$ ^{1e)}, ClF_5 ¹³, ClO_2F ¹² and XeF_6 . ¹⁴ BrF_5 (Matheson) and AsF_5 (Ozark Mahoning) were purified by fractional condensation prior to use. Kr (Matheson) was used without further purification. HF was dried ¹⁵ over BiF_5 (Ozark Mahoning) and treated with $\text{K}_2[\text{NiF}_6]$ (Ozark Mahoning) prior to its use.

Reaction of $\text{Cs}_2[\text{NiF}_6]$ with AsF_5 and ClF_5 . The reaction was carried out in the apparatus depicted in Figure 1. It consisted of a $\frac{3}{4}$ " FEP trap and two $\frac{1}{2}$ " FEP U-traps that were interconnected by Teflon PFA unions containing Teflon filters (Pall Corp.). The apparatus was closed ^{off?} off on both sides by PFA valves that were connected to the stainless steel vacuum line through 1 ft long $\frac{1}{4}$ " FEP tubes.

$\text{Cs}_2[\text{NiF}_6]$ (1.32 mmol) was placed into the $\frac{3}{4}$ " FEP trap and suspended at -60°C in ClF_5 (8.32 mmol). Approximately 5 mL of liquid aHF was condensed into the trap at 60°C . A two-phase system was obtained, consisting of a colorless lower phase (ClF_5) and a dark red upper phase of $\text{Cs}_2[\text{NiF}_6]$ dissolved in aHF. AsF_5 (1.32 mmol) was added to

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Note: Hyphenating the colors is optional. We began annotating hyphens, but you have been consistent in leaving them out, so it's OK to leave them out.

the mixture in four equal increments. After the first addition under vigorous stirring at -60°C , ~~tan~~^Λ-colored NiF_4 was formed. After the second addition and a reaction time of ~~1/2 h~~ ^{0.5 h (or write out half an hour)} at -60 to -40°C , the formation of brown^Λ-violet $\text{Ni}[\text{NiF}_6]$ was observed, while the aHF layer was still dark^Λ-red^Λ-colored. After the addition of the third and fourth increments of AsF_5 and a total reaction time of 14 h at -60 to -10°C , the aHF layer turned pale yellow and the NiF_4 had disappeared. All volatile compounds were removed in a dynamic vacuum at 25°C . The dark^Λ-violet brown residue was suspended in 5 mL aHF at 25°C , and the yellow mother liquor was filtered into U-trap I using 1.5 atm of argon pressure. The aHF was distilled back into the $3/4$ " trap cooled to -196°C under a dynamic vacuum. The residue was stirred with the aHF at 25°C , and the HF solution was filtered again into U-trap I. This procedure was repeated twice. U-trap I containing the aHF solution and U-trap II were cooled with dry ice until a white solid precipitated from the solution in U-trap I. The yellow mother liquor was filtered at -78°C into U-trap II using 1.5 atm of argon pressure. Using the above-mentioned method, the white precipitate was washed twice with aHF at -78°C until the washing solution was only pale yellow in color. The aHF solvent in U-trap II was pumped off, and the solids in the three traps were dried in a dynamic vacuum for 12 h at 25°C .

Based on its color and Raman spectrum, the brown^Λ-violet residue (800 mg) in the $3/4$ " FEP trap consisted of mainly CsAsF_6 ($\nu_1[\text{AsF}_6]^- = 682$ (100); $\nu_2[\text{AsF}_6]^- = 584$ (27); $\nu_5[\text{AsF}_6]^- = 373$ (44) cm^{-1}) and some $\text{Ni}[\text{NiF}_6]$.

The pale yellow solid (200 mg) in U-trap I was mainly $[\text{ClF}_6][\text{AsF}_6]^{10b}$ with $[\text{ClF}_4][\text{AsF}_6]^{16}$ as an impurity (^{19}F NMR: $[\text{ClF}_6]^+ = 385.4$ ppm (6 F, q (1 : 1 : 1 : 1), $^1\text{J}_{19\text{F}} = 338$ Hz); $[\text{ClF}_4]^+ = 385.3$ ppm (6 F, q (1 : 1 : 1 : 1), $^1\text{J}_{19\text{F},37\text{Cl}} = 284$ Hz); $[\text{ClF}_4]^+ =$

273.3 ppm (4F, m); Raman: $\nu_1[\text{ClF}_4]^+ = 817$ (6); $\nu_1[\text{ClF}_6]^+ + \nu_1[\text{AsF}_6]^- = 688.2$ (100); $\nu_2[\text{ClF}_6]^+ = 635$ (11); $\nu_2[\text{AsF}_6]^- = 575$ (15); $\nu_2[\text{ClF}_4]^+ = 569$ (4); $\nu_3[\text{ClF}_6]^+ = 519$ (25); $\nu_3[\text{AsF}_6]^- = 372$ (35) cm^{-1}). According to the ^{19}F NMR data, the composition of the product was $[\text{ClF}_6][\text{AsF}_6]$ (0.52 mmol) and $[\text{ClF}_4][\text{AsF}_6]$ (0.07 mmol).

The yellow residue (228 mg) in U-trap II consisted mainly of $\text{Ni}[\text{AsF}_6]_2$ (vibrations for C_{4v} distorted $[\text{AsF}_6]^-$ in $\text{Ni}[\text{AsF}_6]_2$ ¹⁷ Raman: $\nu_1 = 706$ (41.2); $\nu_3 = 370$ (10) cm^{-1} ; IR: $\nu_8 = 767$ (vs); $\nu_1 = 706$ (m); $\nu_2 = 613$ (vs) cm^{-1} ; the presence of $[\text{Ni}]^{2+}$ was confirmed by the formation of a red colored complex with an aqueous solution of dimethylglyoxime).

The reaction was repeated with $\text{Cs}_2[\text{NiF}_6] = 2.367$ mmol, $\text{AsF}_5 = 11.836$ mmol and $\text{ClF}_5 = 35.508$ mmol at room temperature. After stirring the suspension for 2 d at room temperature, all the $[\text{NiF}_6]^{2-}$ salt was reduced to $\text{Ni}[\text{AsF}_6]_2$. However, on the outer wall of the FEP reaction trap, a yellow film was noted that probably resulted from the plasticization of the Teflon by the reagents and their subsequent hydrolysis. After removing all volatiles at 25 °C, the yellow solid residue was worked up as described above. In contrast ~~of~~^{to} the reaction carried out at -10 °C, the main product isolated was $[\text{ClF}_2\text{O}][\text{AsF}_6]$.¹⁸

$[\text{ClF}_2\text{O}][\text{AsF}_6]$: ^{19}F NMR: $[\text{ClF}_2\text{O}]^+ = 278.4$ ppm (2 F, s); Raman: $\nu_1[\text{ClF}_2\text{O}]^+ = 1330$ (24); $\nu_2[\text{ClF}_2\text{O}]^+ = 759$ (40); $\nu_1[\text{AsF}_6]^- = 675$ (100); $\nu_2[\text{AsF}_6]^- = 563$ (13); $\nu_3[\text{ClF}_2\text{O}]^+ = 510$ (29); $\nu_3[\text{AsF}_6]^- = 370$ (57) cm^{-1} .

Reaction of $\text{Cs}_2[\text{NiF}_6]$ with AsF_5 and BrF_5 . The reaction was carried out in a $\frac{3}{4}$ " FEP tube, which was heat sealed at one end and connected to a PFA T-piece at the

other end. The leg of the T-piece, which formed a 90° angle to the FEP trap, was closed by a PFA valve, while the third leg was closed by a PFA stopper.

$\text{Cs}_2[\text{NiF}_6]$ (1.482 mmol) was suspended in BrF_5 (35.529 mmol) at 25°C . The suspension was frozen at -196°C and AsF_5 (8.894 mmol) was added. The mixture was warmed to 25°C and colorless $[\text{BrF}_4][\text{AsF}_6]$ formed at the wall of the FEP tube. After the suspension was stirred for 5 minutes, it was frozen again at -196°C and aHF (39.180 mmol) was condensed into the reaction vessel. Thawing the mixture under vigorous stirring at 25°C resulted in the formation of a brown-violet solid. The suspension was stirred for 12 h at 25°C . After this time it consisted of yellow mother liquor and a white solid. All volatiles were removed in a dynamic vacuum (12 h at 25°C), leaving behind 2049 mg of a pale yellow residue.

This residue was suspended in approximately 3 mL aHF at -20°C . The yellow mother liquor was siphoned off into a $\frac{1}{2}$ " FEP tube that also contained a PFA T-piece, as described above. For the siphoning step, the PFA stoppers on both reactors were replaced by PFA stoppers, each containing two small holes. Through one of the holes in each Teflon stopper, a small FEP tube (1 mm, o. d.) had been pulled, creating a leak-tight connection between the two vessels. During the whole operation a slow nitrogen flow was passed through the FEP reactors. The mother liquor was then pneumatically transferred ^{from} ~~from~~ one tube into the other by closing the second hole of the Teflon stopper of the reactor that contained the undissolved solid and the mother liquor. After the transfer of the mother liquor, both reactors were immediately evacuated and all volatile material was pumped off. This extraction process was repeated two more times until the

color of the mother liquor was only pale yellow. According to its Raman and ^{19}F NMR spectra, this residue (1103 mg) consisted of mainly CsAsF_6 and some $[\text{BrF}_6][\text{AsF}_6]$.

The yellow solid obtained from the evaporation of the mother liquor was washed three times with aHF at -78°C , using the above-described technique. The washings were collected in a second $\frac{1}{2}$ " FEP tube. The reaction product (180 mg), insoluble in aHF at -78°C , consisted of $[\text{BrF}_6][\text{AsF}_6]$, containing a very small amount of $\text{Ni}[\text{AsF}_6]_2$ as impurity. The yellow product (394 mg) obtained from the evaporation of the washing solutions was $\text{Ni}[\text{AsF}_6]_2$.

$[\text{BrF}_6][\text{AsF}_6]$ ¹¹: ^{19}F NMR: $[\text{}^{79}\text{BrF}_6]^+ = 337.2$ ppm (6 F, q (1 : 1 : 1 : 1), $^1\text{J}_{^{19}\text{F},^{79}\text{Br}} = 1578$ Hz); $[\text{}^{81}\text{BrF}_6]^+ = 337.2$ ppm (6 F, q (1 : 1 : 1 : 1), $^1\text{J}_{^{19}\text{F},^{81}\text{Br}} = 1700$ Hz); Raman: $\nu_1[\text{AsF}_6]^- = 686$ (100); $\nu_2[\text{BrF}_6]^+ = 673$ (14); $\nu_1[\text{BrF}_6]^+ = 662$ (37); $\nu_2[\text{AsF}_6]^- = 574$ (29); $\nu_5[\text{BrF}_6]^+ = 408$ (22); $\nu_5[\text{AsF}_6]^- = 371$ (45) cm^{-1} .

Reaction of $\text{Cs}_2[\text{NiF}_6]$ with AsF_5 and Kr. In a 3 mm, i. d. FEP NMR tube, $\text{Cs}_2[\text{NiF}_6]$ (0.08 mmol) was dissolved in ca. 0.3 mL of aHF at -40°C . The solution was frozen at -196°C , and AsF_5 (0.241 mmol) was condensed into the tube. The mixture was warmed to -78°C , pressurized with 2 atm of Kr, and the tube was heat sealed under vacuum at -196°C . Warming the sample to above -20°C resulted in the formation of $\text{Ni}[\text{NiF}_6]$, but there was no ^{19}F NMR evidence for the formation of $[\text{KrF}][\text{AsF}_6]$.

The reaction was repeated in a stainless steel cylinder, using 15 atm of Kr pressure. Again, no evidence for the formation of $[\text{KrF}][\text{AsF}_6]$ could be obtained.

Reaction of $\text{Cs}_2[\text{NiF}_6]$ with AsF_5 and XeF_6 . In the reaction vessel depicted in Fig. 1, $\text{Cs}_2[\text{NiF}_6]$ (0.287 mmol) was dissolved in aHF at -78°C , and then AsF_5

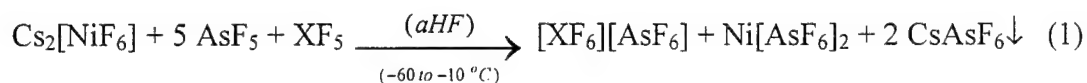
(0.862 mmol) was added at $-196\text{ }^{\circ}\text{C}$. Warming the mixture to $-60\text{ }^{\circ}\text{C}$ resulted in the formation of solid tan-colored NiF_4 and the disappearance of the $[\text{NiF}_6]^{2-}$ anion color from the aHF mother liquor. This suspension was frozen at $-196\text{ }^{\circ}\text{C}$, and XeF_6 (0.862 mmol) was added. The mixture was thawed at $-60\text{ }^{\circ}\text{C}$. At this point, NiF_4 dissolved in the aHF under formation of red-colored $[\text{XeF}_5]_2[\text{NiF}_6]$. This result confirms the observations of Žemva et al.⁶ No evidence for the oxidation of XeF_6 to the $[\text{XeF}_7]^+$ cation was obtained.

Reaction of $\text{Cs}_2[\text{NiF}_6]$ with AsF_5 and ClO_2F . In a 3 mm i. d. FEP tube, $\text{Cs}_2[\text{NiF}_6]$ (0.128 mmol) was suspended in liquid ClO_2F (5.700 mmol) at $-40\text{ }^{\circ}\text{C}$. The suspension was frozen at $-196\text{ }^{\circ}\text{C}$ and AsF_5 (0.640 mmol) was added. Warming the mixture to $-40\text{ }^{\circ}\text{C}$ resulted in the formation of colorless ClO_2AsF_6 ,¹⁹ but in no apparent reaction of $\text{Cs}_2[\text{NiF}_6]$. At $-50\text{ }^{\circ}\text{C}$, a small amount of aHF was added to this mixture. Immediately, the formation of dark violet $\text{Ni}[\text{NiF}_6]$ was observed. The sample was warmed up to $25\text{ }^{\circ}\text{C}$, and all volatiles were removed in a dynamic vacuum. The ^{19}F NMR spectrum of the residue in 0.3 mL aHF at $25\text{ }^{\circ}\text{C}$ gave no evidence for the formation of $[\text{ClO}_2\text{F}_2][\text{AsF}_6]$.²⁰

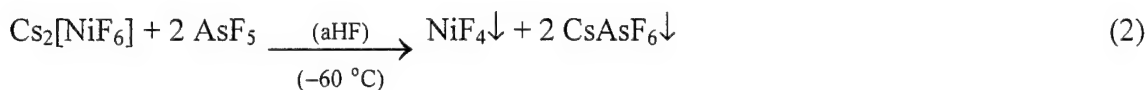
Results and Discussion

Synthesis of $[\text{ClF}_6][\text{AsF}_6]$. The ClF_7 and BrF_7 molecules, the parents of the coordinately saturated complex cations $[\text{ClF}_6]^+$ and $[\text{BrF}_6]^+$, respectively, do not exist. Therefore, the normally facile cation formation by a simple F^- abstraction from the parent molecule using a Lewis acid is not possible. Moreover, ClF_5 and BrF_5 are strong oxidizers, and very strong oxidative fluorinators are needed to prepare the corresponding cations. In view of this, it is not surprising that until now, the formation of the $[\text{ClF}_6]^+$

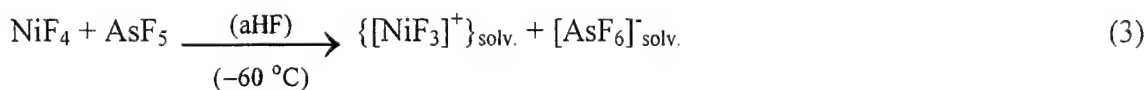
cation had only been achieved by using either $[\text{KrF}]^+$ salts^{10c} or PtF_6 .^{10a,b} The oxidation of BrF_5 had only been attained by using the strongest known oxidizer, the $[\text{KrF}]^+$ cation.¹¹ We have now found that ClF_6AsF_6 and BrF_6AsF_6 can be prepared in 40% and 32 % yield, respectively, from the corresponding halogen pentafluorides and $\text{NiF}_3^+\text{AsF}_6^-$ in anhydrous HF solution, as shown in (1) where X can be Cl or Br.

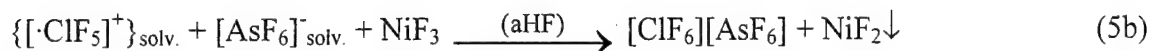
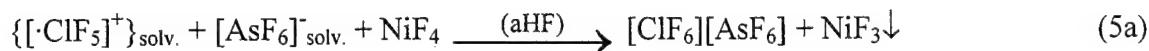
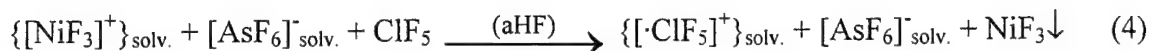


This rather complex reaction involves the following steps. A suspension of $\text{Cs}_2[\text{NiF}_6]$ in ClF_5 forms a two phase system with aHF at -60°C . The colorless lower phase consists of ClF_5 , while the dark red upper phase contains the $\text{Cs}_2[\text{NiF}_6]$ dissolved in aHF. The addition of AsF_5 at -60°C produces at first precipitates of tan colored NiF_4 and colorless CsAsF_6 and is accompanied by the decolorization of the aHF phase (2).



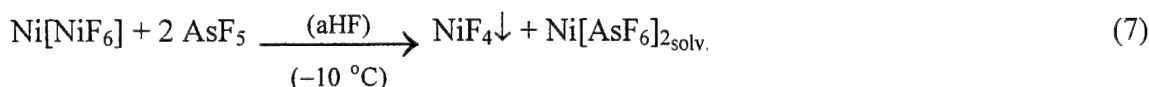
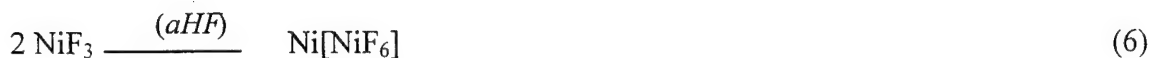
Raising the temperature to -10°C and subsequent addition of more AsF_5 result in a very fast reduction of NiF_4 to brown violet, HF insoluble NiF_3 . The observed oxidation products are $[\text{ClF}_6][\text{AsF}_6]$ and possibly some fluorine. Most likely, NiF_4 forms with AsF_5 an HF soluble $[\text{NiF}_3]^+$ salt (3).⁷ This very powerful oxidizer can act as a one-electron oxidizer and remove an electron from the substrate under formation of NiF_3 and the ClF_5^+ radical cation (4). The latter can react with either NiF_4 or NiF_3 to give the final product $[\text{ClF}_6][\text{AsF}_6]$ (5a or 5b).





This one-electron oxidation mechanism is most plausible because it can explain the formation of NiF_3 . In addition, it is supported by the known reaction of $\text{K}_2[\text{NiF}_6]$ / BF_3 with $[\text{PtF}_6]^-$ salts under formation of PtF_6 ,⁷ the decomposition of NiF_4 to NiF_3 and F_2 ,⁶ and the formation mechanism of NF_4^+ salts,²¹ all of which are best described as one-electron transfer reactions.

After the fast depletion of free NiF_4 , the formed NiF_3 , which is only sparingly soluble in aHF, reacts slowly under the formation of $\text{Ni}[\text{AsF}_6]_2$ and additional $[\text{ClF}_6][\text{AsF}_6]$ at -10°C . This observation can be rationalized by the known tendency of nickel(III)fluoride to disproportionate into Ni(II) and Ni(IV), forming $\text{Ni}[\text{NiF}_6]$ (6).^{2b, 6} In the presence of AsF_5 , the latter forms aHF soluble $\text{Ni}[\text{AsF}_6]_2$ and more NiF_4 (7) that can reenter the oxidation cycle (3) – (5). Since in each cycle, only half of the NiF_4 is consumed, many such cycles are required until essentially all of the $[\text{NiF}_6]^{2-}$ salt is reduced to Ni(II), thus explaining the slowness of this reaction. The low solubilities of NiF_3 and $\text{Ni}[\text{NiF}_6]$ in aHF^{6,22} contribute further to the slowness of the reduction reaction.



Due to the ability of ClF_5 to plasticize the FEP material of the reactor,²³ the reaction should not be performed at higher temperatures or for a longer reaction time. For example, products derived from chlorine oxides and chlorine oxofluorides were detected on the outer wall of the FEP reaction vessel after the reaction of $\text{Cs}_2[\text{NiF}_6]$ with AsF_5 and ClF_5 had been carried out at room temperature for 2 d. The only nonvolatile product in the reactor ~~which~~ ^{that} was identified was $[\text{ClOF}_2][\text{AsF}_6]$,¹⁸ which might have arisen from hydrolysis with a small amount of adventitious water.²⁴

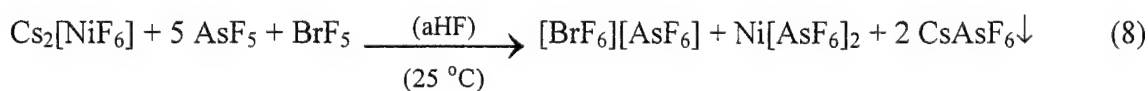
The use of a stainless steel cylinder instead of a FEP reactor, seems to inhibit the formation of $[\text{ClF}_6][\text{AsF}_6]$. This is not surprising ⁵ because the combination of HF with a strong oxidizer is known to rapidly attack metal. This attack results in the formation of $\text{Fe}[\text{NiF}_6]$ as the major product, which is only sparingly soluble in aHF. In contrast to $\text{Ni}[\text{NiF}_6]$, $\text{Fe}[\text{NiF}_6]$ is completely stable at room temperature in aHF and exhibits no pronounced fluorinating abilities.²²

The separation of $[\text{ClF}_6][\text{AsF}_6]$ from the co-products CsAsF_6 and $\text{Ni}[\text{AsF}_6]_2$ can be achieved by suspending the product mixture in HF at 25 °C. At this temperature, CsAsF_6 is the most insoluble component and can be filtered off. At -78 °C, $[\text{ClF}_6][\text{AsF}_6]$ precipitates out from the mother liquor and is filtered off. The filtrate contains $\text{Ni}[\text{AsF}_6]_2$, the most HF [^]soluble reaction product at this temperature. The isolated yield of $[\text{ClF}_6][\text{AsF}_6]$, 40 % based on the limiting reagent $\text{Cs}_2[\text{NiF}_6]$, is higher than that of 11 %

← (Add space)

previously obtained using $[\text{KrF}][\text{AsF}_6]$ as the oxidizer.^{10a} The observed ^{19}F NMR and Raman spectra were in good agreement with previous reports.^{10b,18b}

Synthesis of $[\text{BrF}_6][\text{AsF}_6]$. The oxidizing power of the system $\text{Cs}_2[\text{NiF}_6] / \text{AsF}_5 / \text{aHF}$ is also strong enough to oxidize BrF_5 to $[\text{BrF}_6]^+$. In the absence of HF, the only reaction observed at room temperature was the well-known formation of $[\text{BrF}_4][\text{AsF}_6]$.¹⁶ However, the addition of an equimolar amount of HF relative to BrF_5 resulted in an immediate formation of NiF_4 at -78°C . The solvent HF seems to be essential for this reaction to proceed. Its main function is most likely to solubilize the $\text{Cs}_2[\text{NiF}_6]$. As in the case of ClF_5 , raising of the temperature to 25°C resulted in the initial reduction of NiF_4 to NiF_3 . Due to the much lower vapor pressure of BrF_5 relative to ClF_5 at room temperature, the plasticizing effect of BrF_5 on the FEP material of the reaction vessel is less pronounced. Therefore, the reaction could be performed at 25°C and a complete reduction of the $[\text{NiF}_6]^{2-}$ anion to Ni(II) was attained within 12 h. The observed products were $[\text{BrF}_6][\text{AsF}_6]$, CsAsF_6 and $\text{Ni}[\text{AsF}_6]_2$, as expected for (8).



As in the case of $[\text{ClF}_6][\text{AsF}_6]$, $[\text{BrF}_6][\text{AsF}_6]$ can be isolated by suspending the reaction products in aHF at 25°C . Most of the $[\text{BrF}_6][\text{AsF}_6]$ and all of the $\text{Ni}[\text{AsF}_6]_2$ can be removed from the less HF soluble CsAsF_6 by siphoning off the mother liquor at 25°C . At -78°C , $[\text{BrF}_6][\text{AsF}_6]$ precipitates from the mother liquor, which now contains only $\text{Ni}[\text{AsF}_6]_2$. The yield of $[\text{BrF}_6][\text{AsF}_6]$, based on the limiting reagent $\text{Cs}_2[\text{NiF}_6]$, was 32 % which compares favorably with that of less than 20 % previously reported for the KrF^+

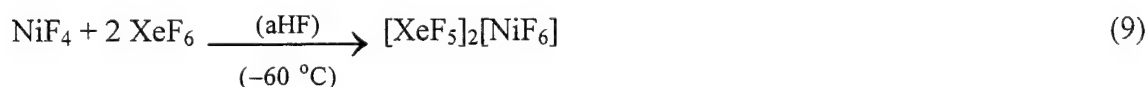
reaction.^{11b} The observed NMR and Raman spectra were in good agreement with the previous reports.¹¹

Reactions of $\text{Cs}_2[\text{NiF}_6]$ / AsF_5 with Kr, XeF_6 and ClO_2F . The successful syntheses of $[\text{ClF}_6][\text{AsF}_6]$ and $[\text{BrF}_6][\text{AsF}_6]$ from $\text{Cs}_2[\text{NiF}_6]$ and AsF_5 in aHF inspired us to investigate further the oxidizing strength and preparative scope of this system. For this purpose we chose Kr, XeF_6 and ClOF_2 as the substrates. Based on the $[\text{F}]^+$ detachment energies of $[\text{FKr}]^+$ and $[\text{XeF}_7]^+$ (115.9 and 116.7 kcal mol⁻¹, respectively)³, the oxidation of Kr and XeF_6 should be more difficult than that of BrF_5 ($[\text{F}]^+$ detachment energy of $[\text{BrF}_6]^+$: 140.8 kcal mol⁻¹).³ However, ClO_2F ($[\text{F}]^+$ detachment energy of $[\text{ClO}_2\text{F}_2]^+$: 161.0 kcal mol⁻¹)³ should be oxidized more easily than BrF_5 .

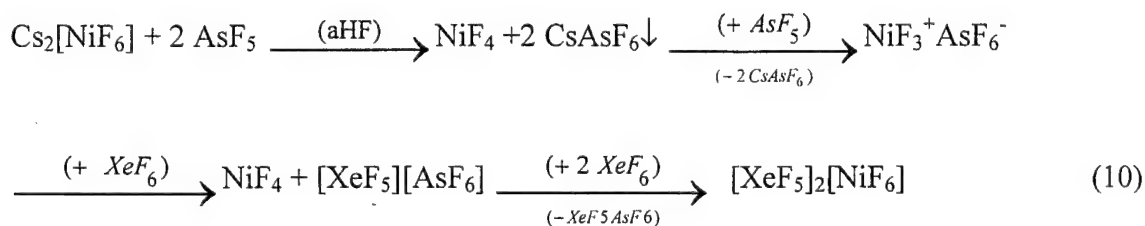
$[\text{KrF}]^+$ salts are the most powerful oxidative fluorinators known today. However, $[\text{KrF}]^+$ salts are rarely used, because KrF_2 is difficult to prepare. The three most widely used methods are: (1) electrical discharge of gaseous mixtures of krypton and fluorine at low temperatures and pressures;²⁵ (2) irradiation of fluorine krypton mixtures by UV or sunlight;^{26,27} and (3) the hot wire method.²⁸ The successful oxidation of Kr, using the system $\text{Cs}_2[\text{NiF}_6]$ / AsF_5 / HF, would provide a convenient and safe synthesis for $[\text{KrF}]^+$ and would reveal, whether this system surpasses the oxidizing strength of $[\text{KrF}]^+$. However, so far $[\text{KrF}]^+$ could not be prepared from $\text{Cs}_2[\text{NiF}_6]$ and AsF_5 in aHF. Reasons for this failure might be either an insufficient oxidizing power of this system or the poor solubility of Kr in HF. An increase of the Kr concentration in aHF can be attained by increasing the Kr pressure. However, the maximum Kr pressure, which can be used in our FEP reactors, is 5 atmospheres. Working under a higher Kr pressure, makes it necessary to carry out the reaction in stainless steel cylinders. This is not practical, due to

the attack of the metal cylinder by the HF/strong oxidizer mixture under formation of transition metal hexafluoronickelates(IV) and $\text{Fe}(\text{AsF}_6)_2$.

Also, it was not possible to oxidize XeF_6 to $[\text{XeF}_7]^+$, using $\text{Cs}_2[\text{NiF}_6]/\text{AsF}_5$ as the oxidizer in aHF. The reason that XeF_6 is not oxidized might be either its high Lewis basicity or an insufficient oxidizer strength of NiF_3^+ . Even if NiF_3^+ is a strong enough oxidizer to oxidize XeF_6 to XeF_7^+ , the high Lewis basicity of XeF_6 could kill the desired reaction by rapidly converting the strong oxidizer NiF_4 back to the more weakly oxidizing $[\text{NiF}_6]^{2-}$ anion, while forming the harder-to-oxidize XeF_5^+ cation. This interpretation is experimentally supported by the observation that, when XeF_6 is added to a freshly prepared suspension of NiF_4 in aHF at -60°C , the tan colored NiF_4 vanishes and the aHF soluble, red colored $[\text{XeF}_5]_2[\text{NiF}_6]$ salt is formed (9).



Reaction (9) was previously used by Žemva et al to verify the formation of NiF_4 .⁶ Although excess AsF_5 could be used to regenerate NiF_4 or the $\{\text{NiF}_3^+\}$ cation, the simultaneous formation of $[\text{XeF}_5][\text{AsF}_6]$ would convert XeF_6 into the more difficult-to-oxidize $[\text{XeF}_5]^+$ cation. Therefore, the observed reaction products of our reaction are best described by the following equations (10).

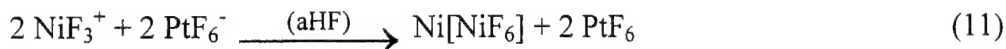


The problems, associated with strongly basic substrates, were confirmed by the reaction of ClO_2F with $\text{Cs}_2[\text{NiF}_6]$ and AsF_5 in aHF. Although, the oxidation of ClO_2F to the $[\text{ClO}_2\text{F}_2]^+$ cation ($[\text{F}]^+$ detachment energy of $[\text{ClO}_2\text{F}_2]^+$: $161.0 \text{ kcal mol}^{-1}$)³ should be easier than that of ClF_5 to the $[\text{ClF}_6]^+$ cation ($[\text{F}]^+$ detachment energy of $[\text{ClF}_6]^+$: $147.3 \text{ kcal mol}^{-1}$)³, the formation of the $[\text{ClO}_2\text{F}_2]^+$ cation was not observed in this reaction. By analogy with XeF_6 , the strongly basic ClO_2F substrate forms with AsF_5 a stable $[\text{ClO}_2][\text{AsF}_6]$ salt, that has no dissociation pressure at room temperature.¹⁹ Under our reaction conditions, all of the ClO_2F is rapidly transformed to $[\text{ClO}_2][\text{AsF}_6]$, which is much harder to oxidize than ClO_2F . Contrary to the reaction of ClO_2F with PtF_6 ,^{10b,c} the formation of small amounts of the $[\text{ClF}_6]^+$ cation as a side-product was not observed. This indicates that under these conditions the $[\text{ClO}_2]^+$ cation is neither oxidized nor undergoes significant oxygen fluorine exchange.

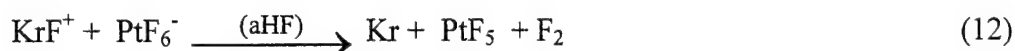
Relative oxidizing strength of NiF_3^+ . Until now $[\text{ClF}_6]^+$ salts were only obtainable from the reaction of ClF_5 with $[\text{KrF}]^+$ salts⁹ or PtF_6 ,¹⁰ and $[\text{BrF}_6]^+$ salts only from the reaction of BrF_5 with $[\text{KrF}]^+$ salts.¹¹ Both, $[\text{ClF}_6][\text{AsF}_6]$ and $[\text{BrF}_6][\text{AsF}_6]$, can be synthesized using NiF_3^+ salts in aHF. According to these results, the NiF_3^+ system is a stronger oxidizer than PtF_6 , because PtF_6 is capable of oxidizing only ClF_5 but not BrF_5 .²¹ This conclusion agrees with the observation that an aHF solution of $\text{K}_2[\text{NiF}_6]$, acidified with BF_3 , oxidizes the $[\text{PtF}_6]^-$ anion to PtF_6 .⁷

A comparison of the oxidizing strengths of NiF_3^+ and KrF^+ is more complicated. Both compounds can oxidize ClF_5 and BrF_5 and, hence, are stronger than PtF_6 that can oxidize only ClF_5 . Although both, NiF_3^+ and KrF^+ , are expected to oxidize the $[\text{PtF}_6]^-$

anion to PtF_6 , the observed reactions are quite different. Whereas NiF_3^+ can act as a one-electron oxidizer towards PtF_6 , resulting in stable NiF_3 or $\text{Ni}(\text{NiF}_6)$ and PtF_6 (11),



KrF^+ behaves as an oxidative fluorinator, oxidizing a δ^- polarized fluoride ligand of PtF_6^- to F_2 (12).



Contrary to NiF_3^+ , which requires only one electron to form stable NiF_3 or $\text{Ni}(\text{NiF}_6)$ and, therefore, can act also as a good one-electron oxidizer, KrF^+ is not a good one-electron oxidizer, because the resulting reduction product, the KrF radical, is unstable and its likely decomposition product, the F radical, is equally unstable. It rather acts like a positive fluorine species, attacking a negatively polarized fluorine ligand under F_2 elimination. Therefore, the chemical characteristics of NiF_3^+ and KrF^+ can be very different and, in our case, do not permit a direct comparison of their relative oxidizer strengths. Consequently, we cannot decide, based on the available information, whether NiF_3^+ or KrF^+ is the stronger oxidizer. Our failure to oxidize Kr with NiF_3^+ to KrF^+ may have been due entirely to unfavorable reaction conditions and does not necessarily imply that KrF^+ is a stronger oxidizer than NiF_3^+ .

Advantages and disadvantages of NiF_3^+ . Compared to PtF_6 , the NiF_3^+ based system offers advantages and disadvantages. On the one hand, the required $\text{K}_2(\text{NiF}_6)_2$, AsF_5 , and HF starting materials are commercially available, and the reaction products are easier to separate than the 1:1 mixture of $\text{ClF}_6^+\text{PtF}_6^-$ and $\text{ClF}_4^+\text{PtF}_6^-$, obtained from the

ClF₅/PtF₆ reaction.²¹ On the other hand, PtF₆ can also oxidize strongly basic substrates, such as ClO₂F,³³ which NiF₃⁺ cannot.

Compared to KrF⁺, the NiF₃⁺ based system again offers commercially available starting materials and higher yields, 40 % for ClF₆⁺ and 32 % for BrF₆⁺, compared to 11^{10c} and < 20 %^{11b} with KrF⁺. However, product isolation and purification is more cumbersome and the final product purity is inferior.

Conclusions

According to our results, the system Cs₂[NiF₆] / AsF₅ / HF should be capable of oxidizing all compounds, that have a higher [F]⁺ attachment energy than BrF₅, provided that the substrate exhibits a lower Lewis basicity than NiF₄. Therefore, a successful oxidation is not only a function of the oxidizing strength but also of the relative Lewis acidities/basicities of all components, because the oxidizing strengths vary significantly from the cation to the neutral parent molecule to the anion.

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Literature

- [1] a) Klemm, W.; Huss, E. *Z. Anorg. Allg. Chem.* **1949**, 253, 221; b) Bodo, H.; Voss, E. *Z. Anorg. Allg. Chem.* **1956**, 286, 136. c) Matwiyoff, A.; Asprey, L. B.; Wageman, W. E.; Reisfeld, M. J.; Fukushima, E. *Inorg. Chem.* **1969**, 8, 750; d) Henkel, H.; Hoppe, R.; Allen, C. G. *J. Inorg. Nucl. Chem.* **1969**, 31, 3855; e) Christe, K. O., *Inorg. Chem.* **1977**, 9, 2238.
- [2] a) Court, T. L.; Dove, M. F. A. *J. Chem. Soc., Chem. Commun.* **1971**, 726; b) Court, T. L.; Dove, M. F. A. *J. Chem. Soc., Dalton* **1973**, 1995.
- [3] Christe, K. O.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, 114, 2978.
- [4] Christe, K. O. *Inorg. Chem.* **1986**, 25, 3722.
- [5] Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1987**, 26, 2554.
- [6] Žemva, B.; Lutar, K.; Chacón, L.; Fele-Beuermann, M.; Allman, J.; Shen, C.; Bartlett, N. *J. Am. Chem. Soc.* **1995**, 117, 10034.
- [7] Lucier, G.; Shen, C.; Casteel Jr., W. J.; Chacón, L.; Bartlett, N. *J. Fluorine Chem.* **1995**, 72, 157.
- [8] Bartlett, N.; Chambers, D.; Roche, A. J.; Spink, R. C. H.; Chacón, L. *J. Chem. Soc., Chem. Commun.* **1996**, 1049.
- [9] Christe, K. O.; Wilson, W. W.; Curtis, E. C. *Inorg. Chem.* **1983**, 22, 3056.

- [10] a) Roberto, F. Q. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 737; b) Christe, K. O. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 741; c) Christe, K. O. *Inorg. Chem.* **1973**, *12*, 1580.
- [11] a) Gillespie, R. J.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1974**, 90; b) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 1230; c) Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1975**, *14*, 694.
- [12] Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.
- [13] Pilipovich, D.; Maya W.; Lawton, E. A.; Bauer, H. F.; Sheehan, D. F.; Ogimachi, N. N.; Wilson, R. D.; Gunderloy, F. C.; Bedwell, V. E. *Inorg. Chem.* **1967**, *6*, 1918.
- [14] Malm, J. G.; Schreiner, F.; Osborne, D. W. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 97.
- [15] Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.
- [16] Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1973**, *12*, 2879.
- [17] Frlec, B.; Gantar, D. *J. Fluorine Chem.* **1982**, *19*, 485.
- [18] a) Christe, K. O.; Curtis, E. C.; Schack, C. J. *Inorg. Chem.* **1972**, *11*, 2212; b) Christe, K. O.; Hon, J. F.; Pilipovich, D. *Inorg. Chem.* **1973**, *12*, 84.
- [19] Christe, K. O.; Schack, C. J.; Pilipovich, D.; Sawodny, W. *Inorg. Chem.* **1969**, *8*, 2489.
- [20] Christe, K. O.; Wilson, R. D.; Curtis, E. C. *Inorg. Chem.* **1973**, *12*, 1358.
- [21] Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1984**, *23*, 2058.
- [22] Shen, C.; Chacón, L.; Bartlett, N. C. *R. Acad. Sci. Paris, t. 2, Série II* **1999**, 557.
- [23] Hensley, W. E.; Walter, R. J.; Chandler, W. T.; Hoffman, N. J., *J. Spacecraft* **1979**, *7*, 174.

- [24] Krasulin, S. V.; Spirin, S. N.; Sokolov, V. B.; Chaivanov B. B. *J. Fluorine Chem.* **1992**, 58, 244.
- [25] Schreiner, F.; Malm, J. G.; Hindman, J. C. *J. Am. Chem. Soc.* **1965**, 87, 25.
- [26] Streng, L. V.; Streng, A. G. *Inorg. Chem.* **1966**, 5, 329.
- [27] Slivnik, J.; Šmalc, A.; Lutar, K.; Žemva, B.; Flec, B. *J. Fluorine Chem.* **1975**, 5, 273.
- [28] Bezmel'nitsyn, V. N.; Legasov, V. A.; Chaivanov, B. B. *Dokl. Akad. Nauk SSSR* **1977**, 235, 96.
- [29] Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1973**, 12, 2879.
- [30] Christe, K. O.; Pilipovich, D. *Inorg. Chem.* **1969**, 8, 391.
- [31] Gillespie, R. J.; Schrobilgen G. J. *Inorg. Chem.* **1974**, 13, 765.
- [32] Weinstock, B.; Claassen, H. H.; Malm, J. G. *J. Am. Chem. Soc.* **1957**, 79, 5832.
- [33] Christe, K. O. *Inorg. Nucl. Chem. Letters* **1972**, 8, 453.
- [34] a) Gillespie, R. J.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1974**, 90; b) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1976**, 15, 22.

Captions for Figures

Figure 1: FEP/PFA reaction vessel

Figure 1

